Remote Femtosecond Laser Induced Breakdown Spectroscopy (LIBS) in a Standoff Detection Regime

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ABSTRACT

The need for robust, versatile, and rapid analysis standoff detection systems has emerged in response to the increasing threat to homeland security. Laser Induced Breakdown Spectroscopy (LIBS) has emerged as a novel technique that not only resolves issues of versatility, and rapid analysis, but also allows detection in settings not currently possible with existing methods. Several studies have shown that femtosecond lasers may have advantages over nanosecond lasers for LIBS analysis in terms of SNR. Furthermore, since femtosecond pulses can travel through the atmosphere as a self-propagating transient waveguide, they may have advantages over conventional stand-off LIBS approaches[1]. Utilizing single and multiple femtosecond pulse laser regimes, we investigate the potential of femtosecond LIBS as a standoff detection technology. We examine the character of UV and visible LIBS from various targets of defense and homeland security interest created by channeled femtosecond laser beams over distances of 30 m or more.

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Keywords: LIBS, femtosecond lasers, filamentation, homeland security

1. Introduction

The detection of energetic materials and explosives in hostile environments has proven to be a complex and challenging problem. In response to this ongoing issue a need to create a rugged system capable of stand off detection and real time analysis has arisen. One technique that has proven its ability to detect all forms of matter with a distinctive spectroscopic signature is that of Laser Induced Breakdown Spectroscopy (LIBS). Many papers have been written in which LIBS has been used to study and characterize solids[2, 3], liquids[4, 5], and gases[6, 7] in a local environment. Applying LIBS to a standoff regime would make it possible to rapidly detect and discriminate explosive and energetic materials from a safe range.

Cremers first demonstrated the LIBS technique for ranged purposes back in 1987.[8] Using laser induced plasma he was able to analyze samples of metals at distances ranging from 0.5 m to 2.4 m using conventional optics and collecting the light into fiber optic cable. Cremers later discovered that LIBS could be performed at a distance of 24 m using

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conventional optics, rather than fiber optics.[9] Expanding upon this work, modern ranged LIBS systems have been used to accurately detect and provide real-time feedback analysis of distances up to and exceeding 80 m utilizing conventional optics.[10]

As more investigations into the remote standoff LIBS frontier are pursued, boundary limitations using a LIBS setup are being determined. These limitations are slowly being pushed back with the advent of new lasers and spectroscopic equipment. Using such techniques that include double pulse and multiple pulse LIBS, researchers have been able to increase their signal to noise ratios thus helping to increase the range detection and characterization. However, as these LIBS systems continue to increase in a range system, they also increase in size, complexity, and cost.

2. Nanosecond LIBS

The Lasema group conducted one of the most definitive tests done to this date using nanosecond LIBS for standoff detection.[11] The results of this experiment illustrated that LIBS has the ability to discriminate finger-print smears of energetic materials (such as TNT) from the substrate and chosen interferents at a specified range. In order to accurately identify the chosen energetic material, it was necessary to identify various elements obtained from a detailed LIBS spectrum such as the one below.

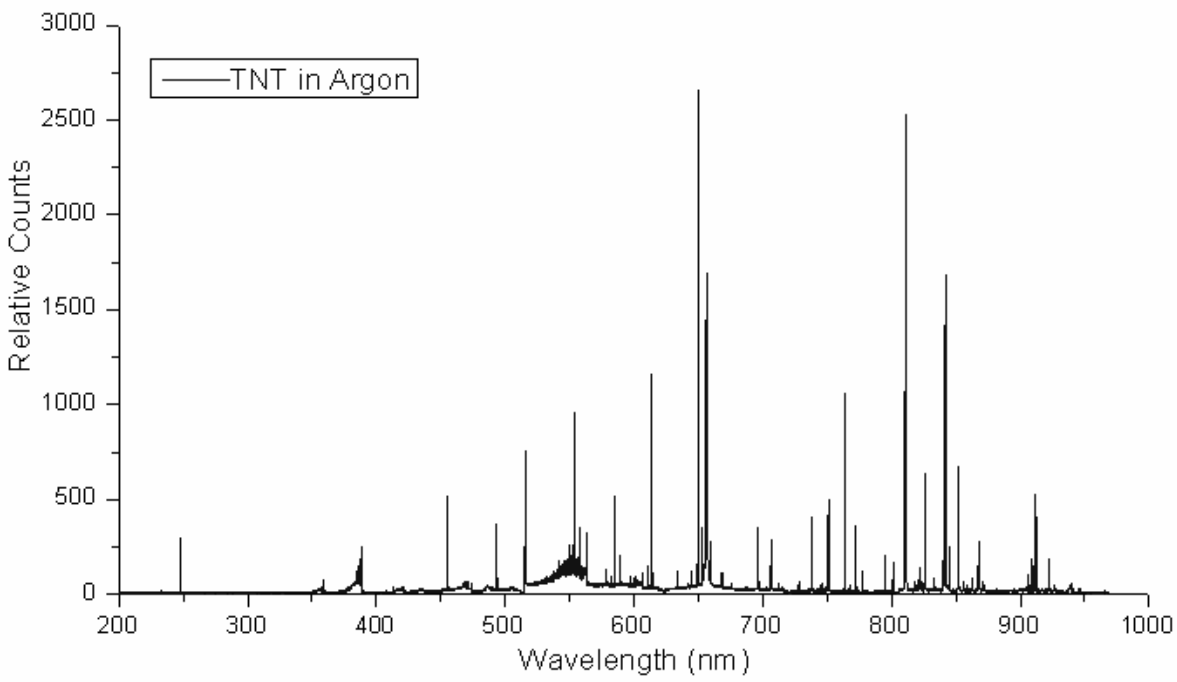

Figure 1: Spectrum of a solid crystal of military grade TNT that was placed on an aluminum substrate and in an environment flooded with argon gas. The spectrum was obtained using a standard Ocean Optics LIBS 2000 system©.

By identifying these lines, atomic and molecular transitions inherent to TNT, as well as identified interferents, containments, and background spectral lines were characterized. A few of the identified spectral lines are displayed below.

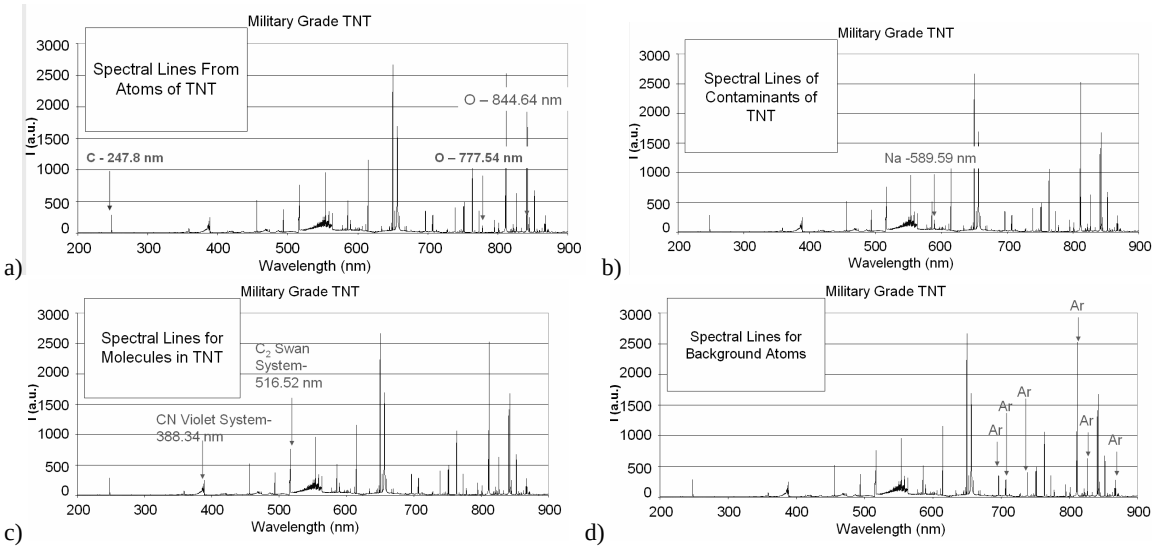

Figure 2: a) Atomic, b) Contaminants, c) Molecular, and d) Background Spectral Lines found in Military Grade TNT.

The results of the LIBS spectrum compared favorably with that of Miziolek et al.[12]

Utilizing the same nanosecond LIBS technique, a similar study was conducted on a hazardous biological sample. Escherichia coli (E. coli) is a bacterial agent that can cause illness and in extreme cases death. It is contagious through a variety of methods, but the most common way is through the ingestion of contaminated meat. Bacillus subtilis (B. subtilis) on the other hand is another bacterium that while contaminating food does not cause food poisoning. In terms of popularity as a laboratory model organism B. subtilis is often used as the Gram-positive equivalent of E. coli, an extensively studied Gram-negative rod.[13] Due to the similarity in nature, we utilized LIBS in order to determine the spectroscopic difference if any between the two bacteria. This experiment was conducted over a five day period, in order to illustrate the whether or not an elapsed period of time would cause enough degradation to the samples, that they could no longer be discriminated by means of spectroscopy. We found that even after a five day period, LIBS was still able to easily identify both samples.

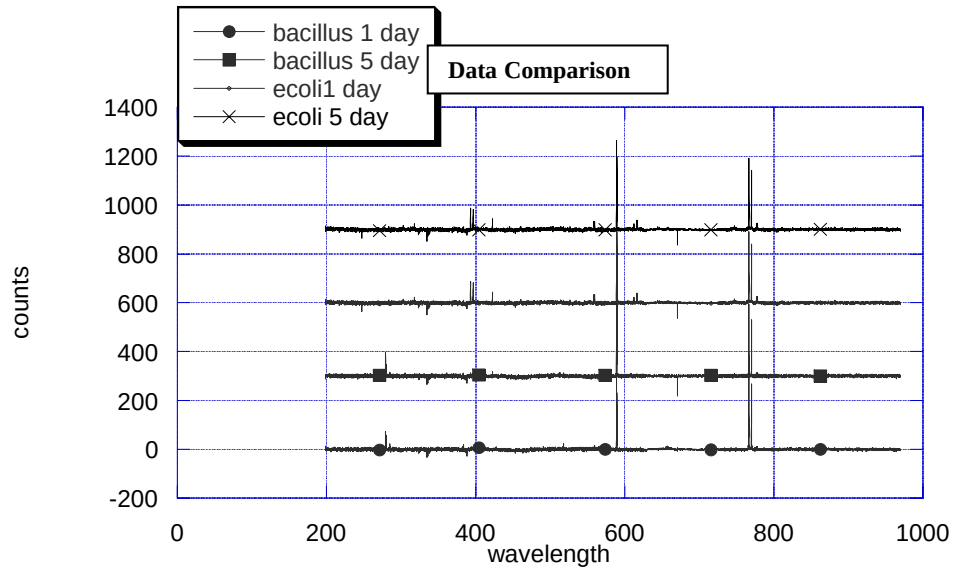

Figure 3: Spectral comparison of E. coli and B. subtilis over a five day period. Negative lines are due to the subtraction of the silver substrate from the spectrum. Single pulse nanosecond LIBS was conducted on the bacteria with an Ocean Optics LIBS 2000 system©.

Since there were no changes evident in the spectrum over time, this suggested that LIBS was a suitable technique for discriminating biological samples. However, studies still need to be completed on how much degradation to the sample is needed before LIBS is no longer a suitable technique by which to identify samples. We then compared our spectroscopic signatures with that A. Samuels et al.[14], and found them to be similar in nature.

After conducting experiments for both chemical and biological agents locally, exploration into technologies that would increase the range and discrimination of nanosecond LIBS was begun. By utilizing Double Pulse LIBS an enhancement of the spectral signature by a factor of 8-10x greater than that of the single pulse LIBS was found, as illustrated below.

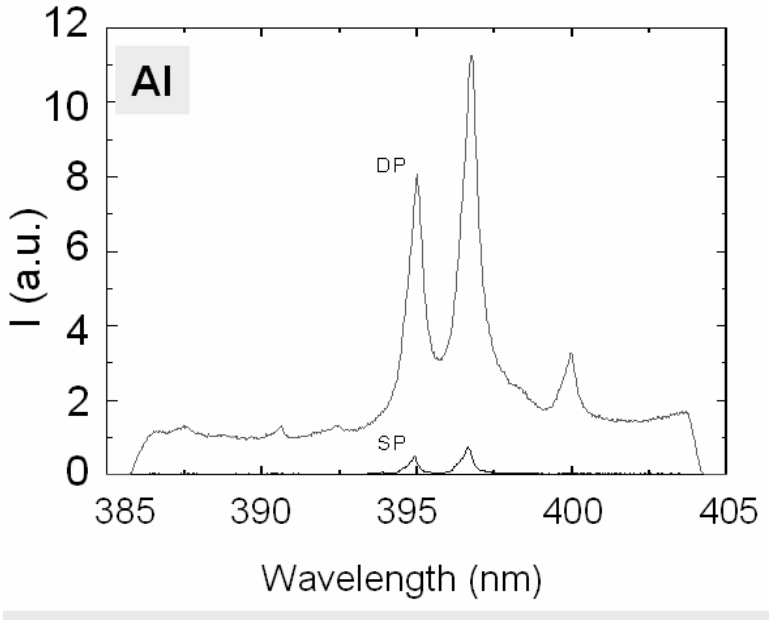

Figure 4: Double Pulse LIB Spectrum compared to a Single Pulse LIB Spectrum for an Aluminum substrate.[14]

While an enhancement factor of 8-10x is considered normal; it was discovered that for some materials, such as stainless steel, a higher enhancement factor may be obtained.

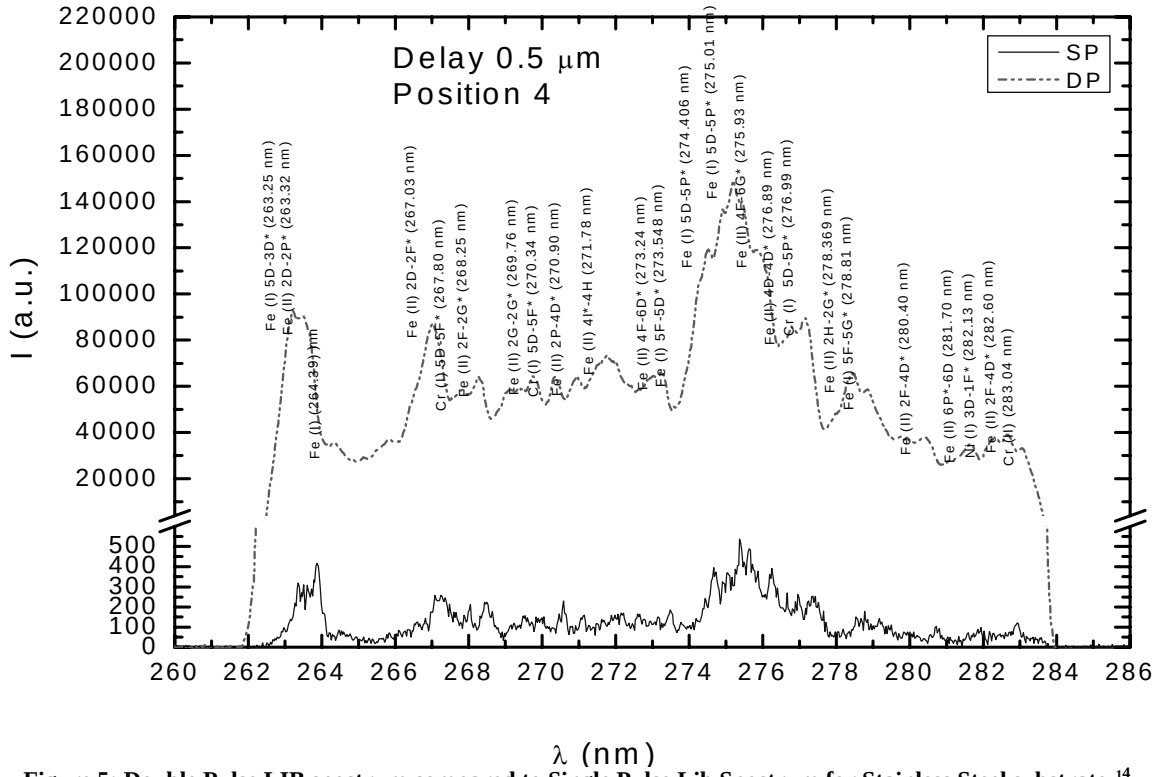

Figure 5: Double Pulse LIB spectrum compared to Single Pulse Lib Spectrum for Stainless Steel substrate. [14]

It is hypothesized that utilizing double pulse LIBS will improve the discrimination of nanosecond LIBS.

While the use of double pulse LIBS improves discrimination, it does not directly address issue of the limited range of nanosecond lasers. Palanco (et al.) has shown that the single pulse nanosecond LIBS signal has a $1/R^5$ dependency as a function of range.[10] This drastic reduction prevented the group from exploring ranges greater than a hundred meters. It must be noted that for most standoff LIBS technology the system utilizes a commercially built laser nanosecond laser. Unfortunately many of the commercial lasers are built for rugged performance and are not necessarily optimized for the far field, and as a consequence the rapid beam divergence leads to larger focused spot sizes.

A larger spot size will require more laser energy to achieve the same intensity on target, a fixed requirement for effective LIBS detection. With low divergence lasers ($M^2 \sim 1$), the reduction in signal as a function of range should diminish by $1/R^3$. Thus the route to larger-range stand-off detection with nanosecond pulses is in part through the use of low divergence lasers and the double-pulse regime. In the latter case the alignment of the two laser focal spots at larger stand-off distances becomes more challenging.

3. **Femtosecond LIBS**

An alternate approach to standoff detection is through the use of femtosecond LIBS. Here one can use the so-called, "self-channeling regime", in which a balance between self-focusing of the intense laser beam in the atmosphere and its consequential partial ionization leads to propagation of the beam as a self-generated microscopic waveguide or filament, thus defying the normal laws of diffraction. In this case we would expect the LIBS signal to have a $1/R^2$ dependency,

There is much still needed to be known on the interaction and LIBS spectral emission from self-channeled femtosecond stand-off LIBS. Although the capability to reduce the 1/R dependence of the LIBS signal is advantageous, it could come with the penalty that the LIBS emission process is limited by the fixed intensity and beam size of the filament ($\sim 10^{14}$ W/cm^2, $\sim 100\mu$m, respectively). One method that might alleviate this limitation, were it to be serious, is the use of burst-

mode fs irradiation[16]. This approach is currently under investigation. Fig. 6 shows comparable spectra from a stainless steel target irradiated with a single pulse and with a train of five pulses of comparable total energy, each separated by ~ 10 ns.

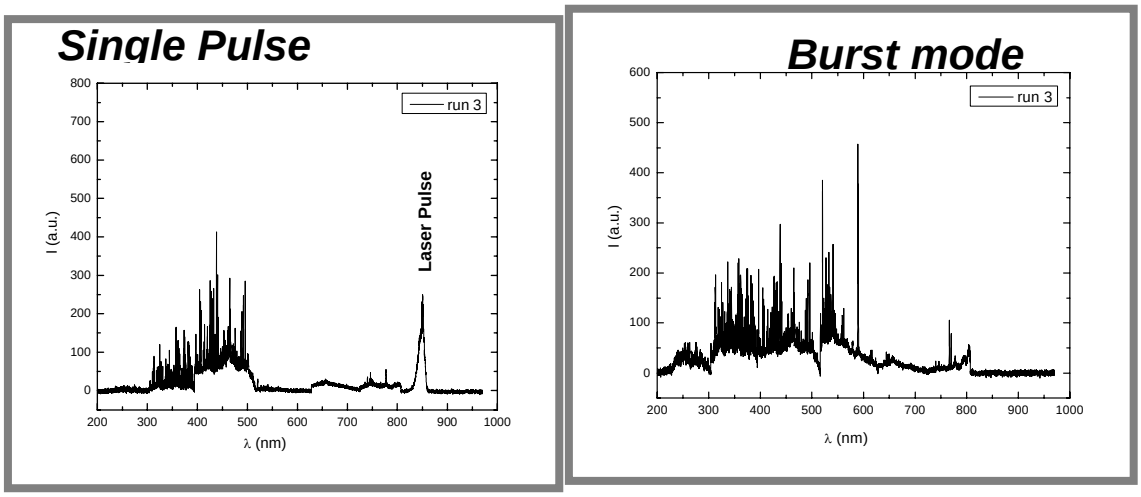

Figure 6: Single Pulse and Burst Mode (Multiple pulse) LIBS conducted on a substrate of stainless steel at a 30 m range. The spectrums were collected using an Ocean Optics LIBS 2000 spectrometer©.

4. Conclusions

Laser Induced Breakdown Spectroscopy (LIBS) is powerful technique that shows promise for the rapid detection and discrimination of many forms matter by a distinct spectral signature. In applying it for stand-off detection, we have discussed several limiting factors, and opportunities for improving signal-to-noise ratios, detectivity and discrimination. Further research will hopefully enable LIBS as an effective stand-off detection technique.

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